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**Polymerization of Ethynyl Pyridinium Triflates,
Ionic Polyacetylenes with Extensively Conjugated Backbones**

by

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POLYMERIZATION OF ETHYNYLPYRIDINIUM TRIFLATES: IONIC POLYACETYLENES WITH EXTENSIVELY CONJUGATED BACKBONES

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Introduction:

Substitution at the backbone carbons of polyacetylene with various groups offers advantages of better processability and greater oxidative stability compared to unsubstituted polyacetylene, but results in substantial lowering of electrical conductivity and third order non linear optical susceptibility (χ^3). This is mainly due to loss of conjugation arising from twisting of the polymer backbone as a result of unfavorable steric interactions between the substituents.

We have recently reported the synthesis of a new class of mono and disubstituted ionic polyacetylenes with extensively conjugated backbones (1-6). The structural features of these polymers are unique with respect to their ionic nature, high degrees of substitution and extensive backbone conjugation. These polymers contain pyridinium ring substituents that are associated with halide or methanesulfonate counterions. The conjugation in these systems despite presence of substituents is attributed to strong electrostatic interactions between the pyridinium ring substituents and the counter ions, which predominates over steric factors that are responsible for twisted backbones(5,6) in uncharged systems.

The polymerization reaction involves activation of the acetylenic triple bond in ethynylpyridines by different methods such as quaternization via a Menschutkin reaction (3,4), formation of donor-acceptor complexes with bromine (5) and by protonation by a strong acid (6). All methods result in transient activated species that undergo spontaneous polymerization, and are limited by relatively low molecular masses (~4000) for the product polymers. This may be attributed to a relatively slow activation step (which results in low concentration of the activated species) compared to rapid propagation and termination steps. In view of this, an alternative method was sought for a more rapid activation of the monomer. Such methods involve use of a highly reactive quaternizing agent that enables the isolation of the activated ethynylpyridinium salt as a stable intermediate.

A new route for polymerization of the acetylenic bond in ethynylpyridines is described. Unlike previous methods wherein quaternization resulted in spontaneous polymerization of the acetylenic bond, the present method affords isolation of the activated monomeric species in the form of alkylpyridinium salts. Polymerization of the activated monomers when initiated with nucleophiles such as pyridine resulted in substituted, ionic polyacetylenes with extensively conjugated backbones. Scheme 1 shows the monomers and proposed structures for the polymers obtained by the present method.



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Experimental:

Materials: 2-Ethynylpyridine and 2-(trimethylsilylethynyl)pyridine were obtained from Farchan Laboratories and distilled under vacuum before use. Trifluoromethane sulfonate was obtained from Aldrich Chemical Company and was used without further purification. Pyridine and DMSO (Aldrich) were distilled before use. **Measurements:** Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrophotometer using KBr plates. UV absorption spectra were obtained at 22° C in DMSO on an IBM 9420 visible-ultraviolet spectrophotometer. Dilute solution viscosity measurements were made in DMSO at 28°C using a Cannon Ubbelohde dilution type viscometer.

N-Methylethynylpyridinium triflates I, II: Were synthesized by the method described by Fife et al. (7) by reacting the ethynylpyridines with an equimolar amount of trifluoromethanesulfonate in anhydrous dichloromethane. The pyridinium salt was purified by recrystallization.

General procedure for polymerization: The activated monomer salt (0.2g) was dissolved in anhydrous DMSO (5ml). This was added to a stirred solution of pyridine (0.002g) in 5ml of DMSO at 20°C. The reaction mixture was stirred for 24 hours and the solvent removed under reduced pressure to yield a dark solid. This was extracted with ether and dried to yield the polymer as a black powder.

Results and Discussion:

The polyacetylenes Ip and IIp obtained from the reaction of monomers I and II respectively with pyridines possess highly conjugated structures as is evident from their absorption spectrum. Both polymers show absorption maxima above 600nm for the unsaturated carbon backbone in the UV visible spectrum. The conjugation lengths are substantially higher than those for the ionic polyacetylenes obtained by previously reported methods. Table 1 shows a comparative list of the absorption maxima for ionic polyacetylenes obtained by us by various activation processes and the conjugation lengths based on theoretical calculations assuming a *trans-transoid* conformation for the polymers (6,8). Molecular dynamics calculations on these systems indicate that this conformation is a stable one for such ionic structures (9). The absorption maxima for both polymers Ia and Ib are close to that of *trans*-polyacetylene (630nm) and are, by far, the highest reported for substituted polyacetylenes. The $\text{C}\equiv\text{C}-\text{H}$ and the $\text{C}\equiv\text{C}$ bands at 3290 and 2109 cm^{-1} respectively in the infrared spectrum of the starting monomer are replaced by a broad band at 3400 cm^{-1} (hydrogen bonded ring C-H) and a strong one at 1612 cm^{-1} (C=C), Figure 1 shows the infra red spectra of monomer I and polymer Ip.

The polymerization of the ethynylpyridinium triflate salts I and II is readily initiated by nucleophiles such as pyridine or triphenyl phosphine. A similar polymerization mechanism has been reported for the corresponding 4-vinylpyridinium triflate salts (7,10). Unlike previous methods the present polymerization involves a non spontaneous process wherein the activation step is separated from the nucleophile initiated polymerization. A possible factor in the termination step due to presence of the excess quaternizing agent is thus avoided. The molecular masses of the resulting polymers is, however, slightly higher than those obtained by spontaneous processes. Optimization of reaction conditions for improvement of molecular masses in these systems is under investigation.

Conclusion:

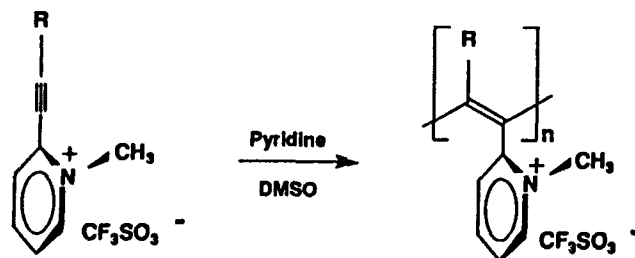
The presently described polymerization reaction of ethynylpyridinium triflates initiated by nucleophiles offers a new route for the synthesis of highly conjugated, substituted polyacetylenes. Unlike the spontaneous processes described previously for the synthesis of such systems, the present method involves isolation of the activated pyridinium salt and a polymerization reaction that is non spontaneous. The resulting polymers have greater conjugation lengths and higher molecular masses than the former methods. Optimization of reaction conditions for improving molecular mass is currently in progress.

Acknowledgement:

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References:

1. Blumstein, A.; Subramanyam, S., *U.S. Patent*, 5,037,916, (1991).
2. Blumstein, A.; Subramanyam, S., *U.S. Patent*, 5,037,916, (1992).
3. Subramanyam, S.; Blumstein, A., *Makromol. Chem. Rapid Commun.*, (1991), **12**, 23.
4. Subramanyam, S.; Blumstein, A., *Macromolecules*, (1991), **24**, 2668.
5. Subramanyam, S.; Blumstein, A., *Macromolecules*, (1992), in press.
6. Subramanyam, S.; Blumstein, A., *Macromolecules*, (1992), in press.
7. Fife, W.K.; Ranganathan, K.; Zeldin, M., *J. Org. Chem.*, (1990), **55**, 5610.
8. Dai, L.; White, J.W., *Polymer*, (1991), **32**(12), 2120.
9. Clough, S.B.; Sun, X.F.; Subramanyam, S.; Blumstein, A.; Tripathy, S.K., *Macromolecules*, submitted.
10. Ranganathan, P.; Fife, W.K.; Zeldin M., *J. Polym. Sci. A*, (1990), **28**, 2711.



I, Ip: R = H

II, IIp: R = S(CH₃)₃

Scheme 1

Table 1. Absorption maxima and conjugation lengths (n) of ionic polyacetylenes synthesized by different methods

| Method | λ_{\max} (C=C) ^a (nm) | n^b (calc.) | $(\eta)_{\text{inh}}^c$ dL/g | Ref. |
|----------------------|---|------------------|---------------------------------|-----------|
| Menschutkin reaction | 440-490 | 4-10 | 0.2 | 3,4 |
| Halogen complex | 450 | 8 | 0.1 | 5 |
| Protonation | 530 | 15 | 0.2 | 6 |
| Triflate salt | 610 | 22 | 0.3 | this work |

^a From UV-vis. spectra in DMSO at 22°C

^b From Lewis Calvin equation (Ref. 8)

^c In absolute methanol and DMSO at 28°C

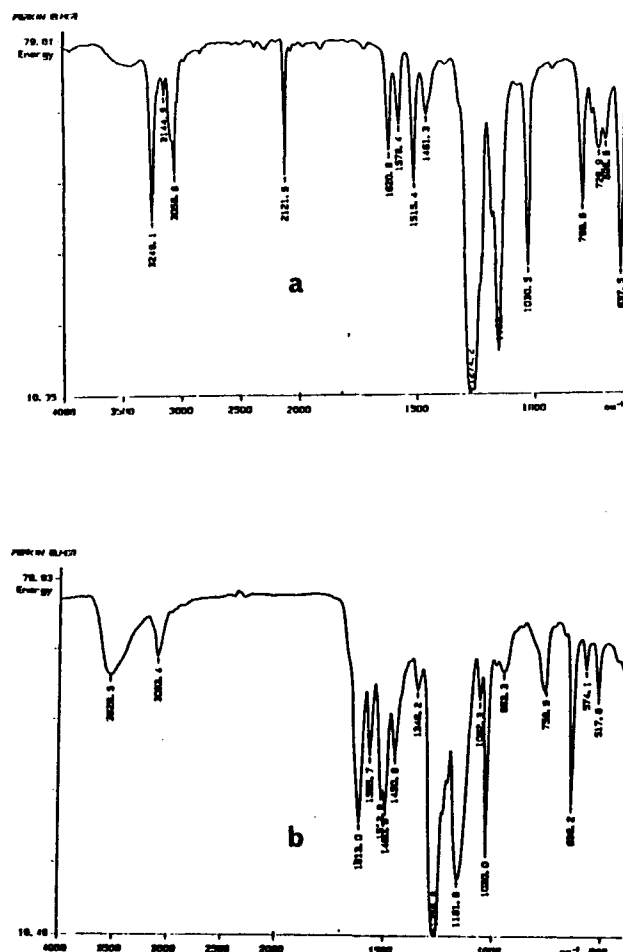


Figure 2: IR spectra of (a) monomer I and (b) polymer Ip